



EUROPEAN PATENT SPECIFICATION

Date of publication of patent specification :
12.06.91 Bulletin 91/24

Int. Cl.⁵ : **C08F 8/28**

Application number : **86870096.4**

Date of filing : **01.07.86**

Cross-linked polyvinyl butyral.

Priority : **02.07.85 US 751116**

Date of publication of application :
25.02.87 Bulletin 87/09

Publication of the grant of the patent :
12.06.91 Bulletin 91/24

Designated Contracting States :
AT BE CH DE FR GB IT LI LU NL SE

References cited :
US-A- 3 597 313
US-A- 3 658 745
US-A- 4 575 540

Proprietor : **Monsanto Company**
Patent Department 800 North Lindbergh
Boulevard
St. Louis Missouri 63167-7020 (US)

Inventor : **Cartier, George Etienne**
167 Hartford Terrace
Springfield, MA 01118 (US)
Inventor : **Farmer, Peter Harrington**
70 Avondale Road
Longmeadow, MA 01106 (US)

Representative : **Ernst, Hubert et al**
Monsanto Services International S.A. Avenue
de Tervuren 270/272
B-1150 Brussels (BE)

EP 0 211 818 B1

Note : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to polyvinyl butyral (PVB) resin and more particularly to (i) selectively cross-linked PVB, (ii) a plasticized sheet formed therefrom and (iii) methods of forming such resin and sheet.

Plasticized PVB sheet is very well known as an intermediate for use with glass or plastic panels (hereinafter called "laminating panels") in laminated safety glass assemblies. It is also well known that the high temperature modulus properties of such a sheet and of the PVB resin from which it is made must be closely controlled for optimum performance. For example, if the resin is too stiff, the power required to melt and extrude it into sheet form may be excessive or the resulting sheet may be difficult to handle and may not provide a quality laminate during preparation of the safety glass assemblies. More specifically, when the sheet is too stiff, visually apparent, undesirable air bubbles can appear in the finished laminate. On the other hand, during lamination at the usual, relatively high (e.g. ca. 192°C) temperatures, it is important that the PVB flow adequately to collapse the sheet and fill the space between the two laminating panels, but not so much as to flow out the edges of the laminate which can occur if the modulus of the sheet is too low. In the past, such a delicate matching of the high temperature properties of the sheet to the laminating conditions has frequently not been possible with the result that the laminating operating conditions had to be inconveniently continuously adapted to the properties of the particular sheet being laminated. To the best of present knowledge, a means to control the high temperature properties of a plasticized PVB sheet has not been available in the past to one of ordinary skill in the art.

EP-A-018 6645 (not published at the date of the present application but claiming two priority dates of 21st December, 1984) describes polyvinylbutyral lightly cross-linked through intermolecular linkages developed through the hydrated form of formaldehyde. The polyvinylbutyral is useful for making interlayer sheet for laminated glass, the light cross-linking affording a means of controlling surface roughness of the interlayer sheet.

US-A-3,658,745 describes an acetalated cross-linked hydrogel capable of imbibing water and micro-molecular water solutes and excluding macromolecular water solutes by the process of swelling upon cooling prepared by reacting a polymer containing a plurality of near neighbour hydroxyl groups or containing hydroxyl groups and ether groups, a monoaldehyde and a dialdehyde, the reagents being initially in a state of homogeneous aqueous solution.

US-A-3,597,313 describes resins for imparting wet-strength to paper, made by copolymerising an unsaturated aliphatic alcoholic monomer with one or more cationic monomers to provide a cationic polymer and reacting the cationic polymer with a polyaldehyde.

SUMMARY OF THE INVENTION

Now improvements have been made in the manufacture of PVB resin and sheet made therefrom which minimize or overcome the aforementioned shortcomings of the prior art.

Accordingly, it is a principal object of this invention to tailor the high temperature modulus of PVB sheet to accommodate various laminating conditions by incrementally selectively increasing the molecular weight of the PVB resin.

Another object is to achieve such PVB molecular weight increase by cross-linking two PVOH chains during or just before the acetalization reaction forming the PVB resin.

Other objects of this invention will in part be obvious and will in part appear from the following description and claims.

The polyvinylbutyral of the invention, and sheet made therefrom, are cross-linked through stable intermolecular diacetal linkages developed through an aldehyde containing at least two aldehyde groups, characterised in that the extent of crosslinking is adequate to increase the viscosity of the polyvinyl butyral by about 2% to about 85% over its viscosity in the absence of such linkages. Stable intermolecular linkages are defined herein as those which, once formed in the PVB, are sufficiently stable as to survive the sheet-shaping process, warehouse storage and the laminating process. Such stable linkages are preferably diacetal linkages developed through an aldehyde containing at least two aldehyde groups.

The invention also comprises a process for increasing the viscosity of polyvinyl butyral which comprises having an aldehyde containing at least two aldehyde groups present as cross-linking agent before or during acetalization of polyvinyl alcohol with butyraldehyde to cross-link the acetalized product through adjacent polyvinyl alcohol chains, characterised in that the crosslinking agent is present at a concentration of about 0.0005 to about 0.20 parts per hundred parts of polyvinyl alcohol.

Also included in the invention is a method of forming polyvinyl butyral sheet which comprises :

a. acetalizing polyvinyl alcohol with butyraldehyde in the presence of an aldehyde containing at least two aldehyde groups as cross-linking agent to produce polyvinyl butyral resin cross-linked through stable inter-

molecular linkages, wherein the crosslinking agent is present at a concentration of about 0.0005 to about 0.20 parts per hundred parts of polyvinyl alcohol.

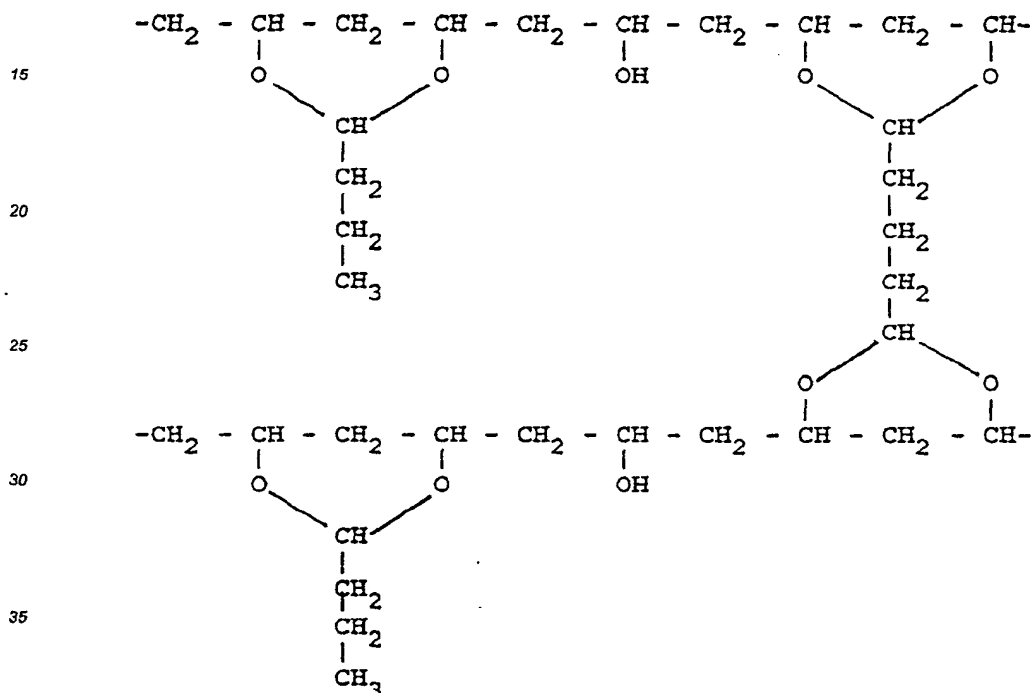
b. mixing said resin with plasticizer and other optional additives to form an extrusion formulation ; and

c. extruding said formulation in melt form through an extrusion opening to form said sheet.

The preferred cross-linking agents are the dialdehydes glutaraldehyde, 4,4(ethylenedioxy)dibenzaldehyde and 2-hydroxyhexanedial.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The PVB lightly cross-linked through diacetal intermolecular linkages has the following formula for a section of polymer chain when employing glutaraldehyde as the cross-linking agent :



As depicted above, the PVB portion of the structure, present at a level of 65-95 weight % of vinyl butyral units in the polymer, is formed through reaction of butyraldehyde with two adjacent hydroxyl groups on the same PVOH chain. The intermolecular cross-linkages (diacetal cross-links) are formed through reaction of one active group of the cross-linking agent (aldehyde) with a pair of adjacent OH groups on one PVOH chain and another active group (also aldehyde) with such a pair of OH's on an adjacent, neighboring chain. By such cross-linking, the PVB molecular weight is conveniently increased in that one cross-link tying together two chains provides the same molecular weight as if two equivalent PVB chains were linked together end to end. The latter is thought to require a difficult synthesis of special, high molecular weight PVOH's and polyvinyl acetate precursors. Yet because such cross-linking is light (to be later defined) and does not join all PVB chains in this manner, some chains being uncross-linked and in the form of conventional PVB polymer units, the molecular weight distribution of the PVB is desirably increased.

In the present invention, as far as the chemical reaction of a cross-linking agent with polyvinyl alcohol to produce intermolecular linkages is concerned, there are no limitations on the choice of the cross-linking agent as long as it contains at least two aldehyde groups capable of interacting with a pair of hydroxyl groups on each of two neighboring PVOH molecular chains to form stable intermolecular linkages which are retained through the melting and extruding operation employed in forming plasticized PVB sheet and the subsequent storage and laminating of such sheet to form safety glass assemblies. Intra-acetal linkages occurring through hydroxyl groups on the same PVB chain are representative of unstable linkages considered to rupture during sheet-shaping or laminating and, if exclusively the means through which cross-linking occurs, are not considered part of

the present invention. Operable cross-linking agents are aldehydes containing at least two CHO groups such as dialdehydes, trialdehydes and the like. The preferred cross-linking agents are dialdehydes, for example, oxaldehyde and the more complex dialdehydes, and trialdehydes containing aliphatic (with or without unsaturation), aromatic or mixed aliphatic/aromatic groups between carbonyl linkages of the CHO groups. Specific functional dialdehydes include aliphatic dialdehydes such as propanedial, succinaldehyde, adipaldehyde, 2-hydroxyhexanedial, etc.; aromatic dialdehydes include phthalaldehyde, 1,4-benzenediacetaldehyde, 4,4'(ethylenedioxy) dibenzaldehyde, 2,6-naphthalene dicarbaldehyde, etc. Operable trialdehydes include N,N',N''-(3,3',3''-) triformylethyl isocyanurate and the like. Mixtures of the foregoing and other cross-linking agents are also suitable. Preferred dialdehydes are selected from the group consisting of glutaraldehyde, 4,4' (ethylenedioxy) dibenzaldehyde and 2-hydroxyhexanedial. The most preferred dialdehyde is glutaraldehyde.

The level of cross-linking should not be so low as to provide no effect on the resulting sheet properties in comparison with sheet made from uncrosslinked PVB but, on the other hand, it should not be so high as to adversely affect sheet properties. For example, at too high a cross-link level the sheet will be too stiff and most likely will perform poorly during handling and laminating. The concentration of cross-linking agent should be adequate to lightly cross-link the PVB resin, by which is meant that the viscosity of such cross-linked resin is about 2% to about 85% greater than such viscosity in the absence of the cross-linkages. As will be apparent, the high temperature properties of a plasticized sheet formed from such a lightly cross-linked PVB resin can be conveniently selectively controlled by the extent of cross-linking or, in other words, by the amount of cross-linking agent available to develop such cross-links. To achieve the viscosity percentage increases stated, the viscosity of the lightly cross-linked PVB resin (7.5 weight % solution in methanol at 20°C.) will be between about 90 cps (0.09 Pa · s) to about 325 cps (0.325 Pa · s) and preferably between about 150-260 cps (0.150-0.260 Pa · s). The concentration of cross-linking agent to provide these cross-linked PVB viscosities will broadly vary with the molecular weight of the cross-linking agent used, the higher the molecular weight of cross-linking agent, the greater the amount required. For the preferred di and trialdehydes, the concentration should be between about 0.0005 to about 0.20 and preferably 0.01 to 0.04 parts per hundred parts of PVOH.

PVOH's useful in this invention are products of the acid or base catalyzed hydrolysis of a polyvinyl ester (usually polyvinyl acetate) which are suitable for the production of PVB resin by condensation with butyraldehyde. Such PVOH's comprise products of a substantially complete as well as incomplete hydrolysis, the latter including those where hydrolysis is purposely stopped short of completion. PVB resin made from such products of incomplete hydrolysis differ in the residual content of polyvinyl ester. Useful PVOH's can contain residues of unhydrolyzed vinyl ester in their molecules in amounts up to 5% by weight (calculated as polyvinyl acetate) although amounts on the order of about 0 to 2.5% by weight of polyvinyl acetate are preferred when the PVB resin is to be used in making interlayer sheeting for safety glass.

Lightly cross-linked PVB resin is produced according to this invention by known aqueous or solvent acetalization processes wherein the PVOH hydrolysis product is reacted with butyraldehyde in the presence of an acid catalyst to produce PVB, followed by neutralization of the catalyst, separation, stabilization and drying of the PVB resin. The cross-linking reaction occurs substantially in conjunction with formation of the PVB resin in this reaction. Depending on its rate of reaction, the cross-linking agent is added to the catalyzed condensation reaction mixture before or simultaneously with the butyraldehyde. In a solvent system, the sequence of addition may be somewhat different; for example, it may be necessary to add the cross-linking agent after the PVB is in solution.

In a solvent process, acetalization is carried out in the presence of sufficient solvent to dissolve the PVB formed and produce a homogeneous solution at the end of acetalization. The PVB is separated from solution by precipitation of solid particles with water which are then washed and dried. Solvents used are lower aliphatic alcohols such as ethanol.

In an aqueous process, acetalization is carried out by adding butyraldehyde to a water solution of PVOH at a temperature on the order of about 20°C., in the presence of an acid catalyst, agitating the mixture to cause an intermediate PVB to precipitate in finely divided form and continuing the agitation while heating until the reaction mixture has proceeded to the desired end point.

The lightly cross-linked PVB resins of the invention have Staudinger molecular weights ranging from about 30,000 to 600,000 and preferably from 45,000 to 270,000 and may be considered to be made up on a weight basis, of from 5 to 30% hydroxyl groups, calculated as polyvinyl alcohol, 0 to 5% ester groups, calculated as polyvinyl ester, and the balance substantially butyral groups. The PVB resin preferably contains, on a weight basis, from 11 to 25% hydroxyl groups, calculated as polyvinyl alcohol, and from 0 to 2.5% acetate groups, calculated as polyvinyl acetate, the balance being substantially butyral groups. The extent of PVB cross-linking in the present invention is so light that the effect on the hydroxyl content of the PVB presently cannot be measured.

In forming the extruded interlayer sheet, the lightly cross-linked PVB resin must be plasticized with from

about 20 to 80 parts plasticizer per hundred parts of resin and more commonly between 25 and 45 parts for conventional laminated safety glass use. This latter concentration is generally used with polyvinyl butyrals containing 17 to 25% vinyl alcohol by weight. In general, plasticizers commonly employed are esters of a polybasic acid or a polyhydric alcohol. Particularly suitable plasticizers are triethylene glycol di-(2-ethyl butyrate), dihexyl adipate, dioctyl adipate, mixtures of heptyl and nonyl adipates, dibutyl sebacate, polymeric plasticizers such as the oil-modified sebacid alkyds, and mixtures of phosphates and adipates such as are disclosed in U.S. No. 3,841,890 and adipates and alkyl benzyl phthalates such as disclosed in U.S. No. 4,144,217. Other suitable plasticizers are well known or will be obvious to those skilled in the art.

The extruded interlayer formed from plasticized, lightly cross-linked PVB resin according to this invention can be prepared by extrusion through a sheeting die, i.e. forcing molten plasticized PVB through a horizontally long, vertically narrow die opening substantially conforming in length and width to that of the sheet being formed therein or by casting molten polymer issuing from an extrusion die onto a specially prepared surface of a die roll positioned in close proximity to the exit of such die which imparts the desired surface characteristics to one side of the molten polymer. Thus, when the surface of such roll has minute peaks and valleys, sheet formed of polymer cast thereon will have a rough surface on the side which contacts the roll which generally conforms respectively to the valleys and peaks of the roll surface. Further details of construction of such a die roll are disclosed in U.S. No. 4,035,549, col. 3, line 46 through col. 4, line 44, the content of which is incorporated herein by reference.

A rough surface on the other side of the extruded interlayer formed in a die roll extrusion system can be provided by the design of the die opening through which the extrudate passes. Such a die opening configuration is generally shown in Fig. 4 of U.S. No. 4,281,980, the content of such figure being incorporated herein by reference. When the outermost end portion of die lip 5 in such figure in the direction of extrusion is parallel with a tangent to the surface of the opposing rotating die roll, and the remaining rearward portion of such lip is at an angle of between about 2 to 7 degrees with such tangent, a rough surface will automatically be generated on the side of the extruded interlayer which is opposite to that formed by the die roll surface.

In addition to plasticizers, interlayers according to this invention may contain other additives such as dyes, ultraviolet light stabilizers, antioxidants, salts to control adhesion and may, if desired, be treated with additives to improve laminating efficiency.

The following procedures were used in obtaining the values for the various properties presented herein :

Melt or complex viscosity of the plasticized, lightly cross-linked PVB with a Rheometric Mechanical Spectrometer at a frequency of 1 hertz. The sample was placed between two parallel plates oscillating at such frequency.

Viscosity by a capillary tube viscometer - Cannon Fenske # 400.

The invention is further described with reference to the following Examples which are for illustration only and are not intended to imply any limitation or restriction on the invention. Unless otherwise indicated, all quantities are expressed by weight.

EXAMPLES 1-3

Polyvinyl alcohol (PVOH) resin having a residual polyvinyl acetate content of less than 2% was dissolved with agitation in water at 90-95°C. to form an 8% solution ; 1250 g of this PVOH solution (100 g of PVOH) was charged to an agitated fluted reactor and its temperature adjusted to 18°C. To this solution was added 70.86 g of butyraldehyde and various amounts (See Table 1 following) of a 50% aqueous solution of glutaraldehyde which decreased the temperature to about 16°C. 5.7 ml of a 35% water solution of nitric acid was then charged and the mixture held for 22-24 minutes at between 16 and 20°C and then heated over 20-30 minutes to 75°C and held thereat for 2.5 h. The contents of the reactor was washed with water at 75°C to a pH of 4.0. Potassium hydroxide water solution was then charged to provide a pH of 9.5-10.5 and the contents held at this pH for 1.5 h at 75°C. Additional water at 75°C was then added to decrease the pH to 7.5. The PVB slurry was centrifuged and dried to less than 2% moisture. The viscosity of the dried PVB resin was measured and the following results were obtained :

TABLE 1

Ex.	Glutaraldehyde charged (g)	PVB viscosity (cps)(Pa.s)
1	0	(175)(0.175)
2	0.06	(215)(0.215)
3	0.12	(310)(0.310)

The foregoing results in Table 1 illustrate the preparation of PVB lightly cross-linked through diacetal intermolecular linkages achieved through the presence of glutaraldehyde at 0.06 and 0.12 parts per hundred parts of PVOH as the cross-linking agent in the acetalization of PVOH with butyraldehyde. That cross-linking occurred is shown by the 23% and 77% increases in the viscosity of the PVB occurring when the minor amount of glutaraldehyde was used in Examples 2 and 3 in comparison with that of control Example 1.

EXAMPLES 4 and 5

These examples illustrate preparation of a plasticized sheet made from the lightly cross-linked PVB of Example 2.

32 parts of dihexyl adipate plasticizer were mixed with 100 parts of the cross-linked PVB resin of Example 2 in a high intensity mixer. The plasticized PVB resin was then melted in an extruder and forced in melt form through a die opening onto the surface of an adjacent rotating die roll of the type previously described which had internal cooling means which regulated the temperature of a die blade in contact with the polymer melt at 104°C. The melt was at 190°C and the pressure of the die was 350-400 psi (2415-2756 kPa). The extruded sheet had a thickness of about 30 mils (0.76 mm) and issued from the die roll at about 457cm per minute. The die lip of the die opening as previously described was formed with a compression angle of about 4 degrees. Each side of the extruded sheet was formed with a rough surface. The melt viscosity of the plasticized cross-linked PVB resin (Example 5) was measured and compared with a control (Example 4) and the following results were obtained :

TABLE 2

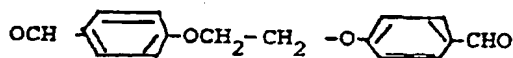
Example	PVB	Melt viscosity (Pa.s) @ 120°C.
4	control	(0.232)(10 ⁵)
5	cross-linked	(0.706)(10 ⁵)

The foregoing results in Table 2 illustrate preparation of plasticized PVB sheet lightly crosslinked through diacetal intermolecular linkages achieved through the presence of glutaraldehyde as the cross-linking agent in forming the PVB from which the sheet was formed. That the cross-links survived the extrusion operation in forming the sheet from the melt is shown by the increased melt viscosity levels obtained with the cross-linked PVB (Example 5) in comparison with the uncross-linked control (Example 4).

EXAMPLE 6

This Example illustrates preparation of a lightly cross-linked PVB using a dialdehyde containing a mixture of aliphatic and aromatic groups between the carbonyl end groups of the dialdehyde.

The PVOH solution used in Example 1 was charged to the reactor of Example 1 and 3.8 ml. of nitric acid (35% aqueous) and 0.17 g of 4,4' (ethylenedioxy) dibenzaldehyde, i.e.



added thereto. This dialdehyde was obtained commercially from Aldrich Chemical Company of Milwaukee, Wis. The reaction mixture was heated to 90°C. over 40 min. and held at 90°C. for 40 min. The solution was then cooled to 20°C. and 67.8 g of butyraldehyde was quickly added with agitation. The reaction mixture was held at this temperature for 40 min. and then heated to 75°C. over a period of 20 min. The remaining conditions and treatment of the resulting product were identical to those described in Examples 1-3. The viscosity of the lightly cross-linked PVB resin obtained was 220 cps (0.220 Pa · s which is about 26% greater than that of the uncross-linked control of Example 1. The sequential cross-linking of the PVOH followed by acetalization with butyraldehyde was necessary because of the reduced reactivity of the larger, bulkier dialdehyde of this Example. It is believed that a plasticized PVB sheet could be formed from this cross-linked PVB by following the procedure of Example 5.

EXAMPLE 7

This Example illustrates preparation of a lightly cross-linked PVB using a long chain aliphatic dialdehyde containing a substituted hydroxyl between carbonyl end groups of the dialdehyde.

The procedure of Example 6 was repeated except that 0.33 g of a 25% aqueous solution of 2-hydroxyhexanedial from Aldrich Chemical Co. i.e.

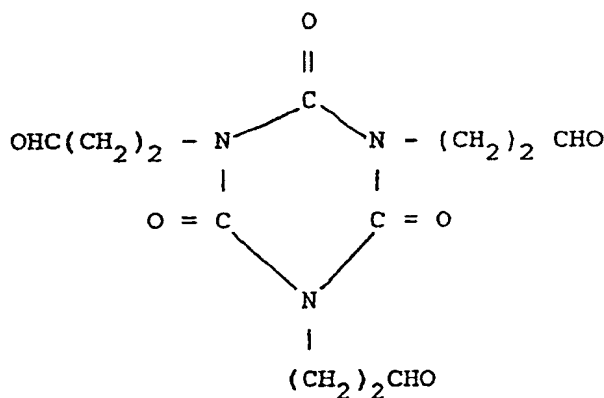


was added to the PVOH-nitric acid mixture instead of the dialdehyde used in Example 6. The reaction mixture was held at 90°C. for 30 min. before cooling to 20°C. Butyraldehyde (67.8 g) was then added as in Example 6 and the reaction mixture held at 20°C. for 52 min before heating to 75°C. The remaining reaction conditions and treatment of the resulting product were identical to those described in Example 6. The viscosity of the cross-linked PVB resin obtained was 318 cps (0.318 Pa · s which is about 82% greater than that of the uncross-linked control of Example 1. It is believed that a plasticized PVB sheet could be formed from this cross-linked PVB by following the procedure of Example 5.

EXAMPLE 8

This Example illustrates preparation of a cross-linked PVB using a trialdehyde as the agent cross-linking the intermolecular PVOH chains.

The procedure of Example 6 was repeated except that 0.36 g of a 50% aqueous solution of N,N',N''-(3,3',3'' triformylethyl) isocyanate prepared according to U.S. Patent No. 4,293,693, i.e.



was added to the PVOH-nitric acid mixture instead of the dialdehyde used in Example 7. The remaining procedure, temperatures and amounts of constituents were identical to Example 6. The viscosity of the PVB resin

obtained was 300.5 cps (0.3005 Pa · s which is about 72% greater than that of the uncross-linked control of Example 1. It is believed that a plasticized PVB sheet could be formed from this lightly cross-linked PVB by following the procedure of Example 5.

5 EXAMPLE 9

The procedure of Example 1 was repeated except that i) the PVOH was initially dissolved in water at 105°C and to the solution was added 62.1 g of butyraldehyde and 0.018 g of a 50% aqueous solution of glutaraldehyde, ii) after addition of the nitric acid catalyst the mixture was heated to 85°C and held at this temperature for 4 h and iii) after addition of potassium hydroxide, the PVB slurry was held at 85°C for 1.5 h. The viscosity of the dried PVB resin obtained was 288 cps or 0.288 Pa · s.

The preceding description is set forth for purposes of illustration only and is not to be taken in a limited sense. Various modifications and alterations will be readily suggested to persons skilled in the art. It is intended, therefore, that the foregoing be considered as exemplary only and that the scope of the invention be ascertained from the following claims.

Claims

1. Polyvinyl butyral cross-linked through stable intermolecular diacetal linkages developed through an aldehyde containing at least two aldehyde groups, characterised in that the extent of cross-linking is adequate to increase the viscosity of the polyvinyl butyral by about 2% to about 85% over its viscosity in the absence of such linkages.
2. A polyvinyl butyral of Claim 1, wherein the diacetal linkages are developed through a trialdehyde or a dialdehyde containing an aliphatic or an aromatic group or a mixture of aliphatic and aromatic groups between carbonyl groups.
3. A polyvinyl butyral of Claim 1, wherein the intermolecular linkages are developed through a dialdehyde selected from glutaraldehyde, 4,4'-(ethylenedioxy)dibenzaldehyde and 2-hydroxyhexanedial.
4. A polyvinyl butyral of Claim 1, wherein the intermolecular linkages are developed through a trialdehyde.
5. A polyvinyl butyral of Claim 1, wherein the diacetal linkages are developed through glutaraldehyde.
6. A sheet of plasticized polyvinyl butyral crosslinked through stable intermolecular diacetal linkages developed through an aldehyde containing at least two aldehyde groups, characterised in that the extent of cross-linking is adequate to increase the viscosity of plasticized polyvinyl butyral by about 2 to about 85% over its viscosity in the absence of such linkages.
7. A sheet of Claim 6, wherein the diacetal linkages are developed through a trialdehyde or a dialdehyde containing an aliphatic or an aromatic group or a mixture of aliphatic and aromatic groups between carbonyl groups.
8. A sheet of Claim 6, wherein the intermolecular linkages are developed through a dialdehyde selected from glutaraldehyde, 4,4'-(ethylenedioxy) dibenzaldehyde and 2-hydroxyhexanedial.
9. A sheet of Claim 6, wherein the intermolecular linkages are developed through glutaraldehyde.
10. A process for increasing the viscosity of polyvinyl butyral, which comprises having a dialdehyde or a trialdehyde present as cross-linking agent before or during acetalization of polyvinyl alcohol with butyraldehyde to cross-link the acetalized product through adjacent polyvinyl alcohol chains, characterised in that the crosslinking agent is present at a concentration of about 0.0005 to about 0.20 parts per hundred parts of polyvinyl alcohol.
11. A process of Claim 10, wherein the cross-linking agent is a trialdehyde or a dialdehyde containing an aliphatic or an aromatic group or a mixture of aliphatic and aromatic groups between carbonyl groups.
12. A process of Claim 11, wherein the cross-linking agent is a trialdehyde.
13. A process of Claim 11, wherein the cross-linking agent is selected from glutaraldehyde, 4,4'-(ethylenedioxy) dibenzaldehyde and 2-hydroxyhexanedial.
14. A process of Claim 13, wherein the aldehyde is glutaraldehyde.
15. A process of any of Claims 10 to 14, wherein the polyvinyl butyral contains 65 to 95 weight percent of vinyl butyral units.
16. A method of forming polyvinyl butyral sheet which comprises :
 - a. acetalizing polyvinyl alcohol with butyraldehyde in the presence of a dialdehyde or a trialdehyde as cross-linking agent to produce polyvinyl butyral resin cross-linked through stable intermolecular linkages ; where in the cross-linking agent is present at a concentration of about 0.0005 to about 0.20 parts per hundred parts of polyvinyl alcohol.

- b. mixing said resin with plasticizer and other optional additives to form an extrusion formulation ; and
- c. extruding said formulation in melt form through an extrusion opening to form said sheet.

17. A method of Claim 16, wherein the cross-linking agent is a trialdehyde or a dialdehyde which contains an aliphatic or an aromatic group or a mixture of aliphatic and aromatic groups between carbonyl groups.

5 18. A method of Claim 17, wherein the cross-linking agent is selected from glutaraldehyde, 4,4'-(ethylene-dioxy) dibenzaldehyde and 2-hydroxyhexanedial.

19. The method of Claim 18 wherein the cross-linking agent is glutaraldehyde.

10 Ansprüche

1. Polyvinylbutyral vernetzt durch stabile intermolekulare Diacetalverknüpfungen, die durch einen Aldehyd mit mindestens zwei Aldehydgruppen entwickelt sind, dadurch gekennzeichnet, daß das Ausmaß der Vernetzung adäquat ist, um die Viskosität des Polyvinylbutyrals um etwa 2 bis etwa 85% gegenüber seiner Viskosität in Abwesenheit derartiger Verknüpfungen zu erhöhen.

2. Polyvinylbutyral nach Anspruch 1, in dem die Diacetalverknüpfungen durch einen Trialdehyd oder einen Dialdehyd mit einer aliphatischen oder einer aromatischen Gruppe oder einer Mischung von aliphatischen und aromatischen Gruppen zwischen Carbonylgruppen entwickelt sind.

3. Polyvinylbutyral nach Anspruch 1, in dem die intermolekularen Verknüpfungen durch einen Dialdehyd ausgewählt aus Glutaraldehyd, 4,4'-(Äthylendioxy)-dibenzaldehyd und 2-Hydroxyhexandial entwickelt sind.

4. Polyvinylbutyral nach Anspruch 1, in dem die intermolekularen Verknüpfungen durch einen Trialdehyd entwickelt sind.

5. Polyvinylbutyral nach Anspruch 1, in dem die Diacetalverknüpfungen durch Glutaraldehyd entwickelt sind.

6. Folie aus weichgemachtem Polyvinylbutyral, vernetzt durch stabile intermolekulare Diacetalverknüpfungen, die durch einen Aldehyd mit mindestens zwei Aldehydgruppen entwickelt sind, dadurch gekennzeichnet, daß das Ausmaß der Vernetzung adäquat ist, um die Viskosität des weichgemachten Polyvinylbutyrals um etwa 2 bis etwa 85% gegenüber seiner Viskosität in Abwesenheit derartiger Verknüpfungen zu erhöhen.

7. Folie nach Anspruch 6, in der die Diacetalverknüpfungen durch einen Trialdehyd oder einen Dialdehyd mit einer aliphatischen oder einer aromatischen Gruppe oder einer Mischung von aliphatischen und aromatischen Gruppen zwischen Carbonylgruppen entwickelt sind.

8. Folie nach Anspruch 6, in der die intermolekularen Verknüpfungen durch einen Dialdehyd ausgewählt aus Glutaraldehyd, 4,4'-(Äthylendioxy)-dibenzaldehyd und 2-Hydroxyhexandial entwickelt sind.

9. Folie nach Anspruch 6, in der die intermolekularen Verknüpfungen durch Glutaraldehyd entwickelt sind.

10. Verfahren zum Erhöhen der Viskosität von Polyvinylbutyral, bei dem ein Dialdehyd oder ein Trialdehyd als Vernetzungsmittel vor oder während der Acetalisierung von Polyvinylalkohol mit Butyraldehyd vorhanden ist, um das acetalisierte Produkt durch benachbarte Polyvinylalkoholketten zu vernetzen, dadurch gekennzeichnet, daß das Vernetzungsmittel in einer Konzentration von etwa 0,0005 bis etwa 0,20 Teilen pro 100 Teile Polyvinylalkohol vorhanden ist.

11. Verfahren nach Anspruch 10, in dem das Vernetzungsmittel ein Trialdehyd oder ein Dialdehyd mit einer aliphatischen oder einer aromatischen Gruppe oder einer Mischung von aliphatischen und aromatischen Gruppen zwischen Carbonylgruppen ist.

12. Verfahren nach Anspruch 11, in dem das Vernetzungsmittel ein Trialdehyd ist.

13. Verfahren nach Anspruch 11, in dem das Vernetzungsmittel ausgewählt ist aus Glutaraldehyd, 4,4'-(Äthylendioxy)-dibenzaldehyd und 2-Hydroxyhexandial.

14. Verfahren nach Anspruch 13, in dem der Aldehyd Glutaraldehyd ist.

15. Verfahren nach einem der Ansprüche 10 bis 14, in dem das Polyvinylbutyral 65 bis 95 Gew.% Vinylbutyraleinheiten enthält.

16. Verfahren zum Herstellen einer Polyvinylbutyralfolie, das umfaßt :

a. das Acetalisieren von Polyvinylalkohol mit Butyraldehyd in Anwesenheit eines Dialdehyds oder eines Trialdehyds als Vernetzungsmittel zum Bilden von Polyvinylbutyralharz, das durch stabile intermolekulare Verknüpfungen vernetzt ist, wobei das Vernetzungsmittel in einer Konzentration von etwa 0,0005 bis etwa 0,20 Teilen pro 100 Teile Polyvinylalkohol vorhanden ist,

b. das Mischen des Harzes mit einem Weichmacher und anderen gegebenenfalls möglichen Additiven unter Bildung einer Extrusionsformulierung und

c. das Extrudieren der Formulierung in Form einer Schmelze durch eine Extrudieröffnung unter Bildung der Folie.

17. Verfahren nach Anspruch 16, in dem das Vernetzungsmittel ein Trialdehyd oder ein Dialdehyd mit einer

aliphatischen oder einer aromatischen Gruppe oder einer Mischung von aliphatischen und aromatischen Gruppen zwischen Carbonylgruppen ist.

18. Verfahren nach Anspruch 17, in dem das Vernetzungsmittel ausgewählt ist aus Glutaraldehyd, 4,4'-(Äthylendioxy)-dibenzaldehyd und 2-Hydroxyhexanedial.

19. Verfahren nach Anspruch 18, in dem das Vernetzungsmittel Glutaraldehyd ist.

Revendications

1. Butyral de polyvinyle réticulé par des liaisons diacétal intermoléculaires stables établies grâce à un aldéhyde contenant au moins deux groupes aldéhyde, caractérisé en ce que le degré de réticulation permet d'augmenter la viscosité du butyral de polyvinyle d'environ 2% à environ 85% par rapport à sa viscosité en l'absence de ces liaisons.

2. Butyral de polyvinyle selon la revendication 1, dans lequel les liaisons diacétal sont établies par l'intermédiaire d'un trialdéhyde ou d'un dialdéhyde contenant un groupe aliphatique ou un groupe aromatique ou un mélange de groupes aliphatiques et aromatiques entre des groupes carbonyle.

3. Butyral de polyvinyle selon la revendication 1, dans lequel les liaisons intermoléculaires sont établies par un dialdéhyde choisi parmi le glutaraldéhyde, le 4,4'-(éthylendioxy)dibenzaldéhyde et le 2-hydroxyhexanedial.

4. Butyral de polyvinyle selon la revendication 1, dans lequel les liaisons intermoléculaires sont établies par un trialdéhyde.

5. Butyral de polyvinyle selon la revendication 1, dans lequel les liaisons diacétal sont établies par du glutaraldéhyde.

6. Feuille de butyral de polyvinyle plastifié réticulé par des liaisons diacétal intermoléculaires stables établie par un aldéhyde contenant au moins deux groupes aldéhyde, caractérisée en ce que le degré de réticulation est adéquat pour augmenter la viscosité du butyral de polyvinyle plastifié d'environ 2 à environ 85% par rapport à sa viscosité en l'absence de ces liaisons.

7. Feuille selon la revendication 6, dans laquelle les liaisons diacétal sont établies par un trialdéhyde ou un dialdéhyde contenant un groupe aliphatique ou un groupe aromatique ou un mélange de groupes aliphatiques et aromatiques entre des groupes carbonyle.

8. Feuille selon la revendication 6, dans laquelle les liaisons intermoléculaires sont établies par un dialdéhyde choisi parmi le glutaraldéhyde, le 4,4'-(éthylendioxy)dibenzaldéhyde et le 2-hydroxyhexanedial.

9. Feuille selon la revendication 6, dans laquelle les liaisons intermoléculaires sont établies par du glutaraldéhyde.

10. Procédé pour augmenter la viscosité du butyral de polyvinyle qui comprend le fait d'avoir un dialdéhyde ou un trialdéhyde présent comme agent de réticulation avant ou pendant l'acétalisation de l'alcool polyvinylique avec du butyraldéhyde pour réticuler le produit acétalisé par l'intermédiaire de chaînes d'alcool polyvinylique adjacentes, caractérisé en ce que l'agent de réticulation est présent à une concentration d'environ 0,0005 à environ 0,20 partie pour 100 parties d'alcool polyvinylique.

11. Procédé selon la revendication 10, dans lequel l'agent de réticulation est un trialdéhyde ou un dialdéhyde contenant un groupe aliphatique ou aromatique ou un mélange de groupes aliphatiques et aromatiques entre des groupes carbonyle.

12. Procédé selon la revendication 11, dans lequel l'agent de réticulation est un trialdéhyde.

13. Procédé selon la revendication 11, dans lequel l'agent de réticulation est choisi parmi le glutaraldéhyde, le 4,4'-(éthylendioxy)dibenzaldéhyde et le 2-hydroxyhexanedial.

14. Procédé selon la revendication 13, dans lequel l'aldéhyde est le glutaraldéhyde.

15. Procédé selon l'une quelconque des revendications 10 à 14, dans lequel le butyral de polyvinyle contient 65 à 95% en poids de motifs butyral de vinyle.

16. Procédé de formation d'une feuille de butyral de polyvinyle qui comprend :

a. l'acétalisation de l'alcool polyvinylique avec le butyraldéhyde en présence d'un dialdéhyde ou d'un trialdéhyde comme agent de réticulation pour produire une résine de butyral de polyvinyle réticulée par des liaisons intermoléculaires stables ; dans laquelle l'agent de réticulation est présent à une concentration d'environ 0,0005 à environ 0,20 partie pour 100 parties d'alcool polyvinylique ;

b. le mélange de cette résine avec un plastifiant et d'autres additifs facultatifs pour former une formule d'extrusion ; et

c. l'extrusion de cette formule sous forme de masse fondue à travers une ouverture d'extrusion pour former cette feuille.

17. Procédé selon la revendication 16, dans lequel l'agent de réticulation est un trialdéhyde ou un dialdé-

hyde qui contient un groupe aliphatique ou un groupe aromatique ou un mélange de groupes aliphatiques et aromatiques entre les groupes carbonyle.

18. Procédé selon la revendication 17, dans lequel l'agent de réticulation est choisi parmi le glutaraldéhyde, le 4,4'-(éthylènedioxy)dibenzaldéhyde et le 2-hydroxyhexanedial.

5 19. Procédé selon la revendication 18, dans lequel l'agent de réticulation est le glutaraldéhyde.

10

15

20

25

30

35

40

45

50

55

International Application No.
PCT/EP 02/03218

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F8/28 C08K5/1535

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 211 818 A (MONSANTO COMPANY) 25 February 1987 (1987-02-25) cited in the application page 1, line 3 - page 2, line 3 page 5, line 9 - page 6, line 17 page 8, line 21 - page 9, line 27 page 10, line 28 - page 11, line 6; claims 1-30	1
A	DE 43 30 354 A (HENKEL) 9 March 1995 (1995-03-09) page 3, line 23 - line 37; claims 1-11	1
A	US 2 448 260 A (N. W. FLODIN) 31 August 1948 (1948-08-31) column 3, line 32 - column 6, line 1; claims 1-4	1

-/-

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed by group.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document relating to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *Z* document member of the same patent family

Date of the actual completion of the international search

24 September 2002

Date of mailing of the international search report

02/10/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5018 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-2016

Authorized officer

Permentier, W

INTERNATIONAL SEARCH REPORT

PCT/EP 02/03218

[illegible]

Information on patent family members

International Application No
PCT/EP 02/03218

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 211818	A	25-02-1987	AT 64401 T	15-06-1991
			AU 581092 B2	09-02-1989
			AU 5943486 A	08-01-1987
			CA 1276744 A1	20-11-1990
			DE 3679737 D1	18-07-1991
			EP 0211818 A1	25-02-1987
			JP 2594243 B2	25-03-1997
			JP 8231639 A	10-09-1996
			JP 2523282 B2	07-08-1996
			JP 62010106 A	19-01-1987
			MX 165554 B	23-11-1992
			US 4902464 A	20-02-1990
			US 4874814 A	17-10-1989
			US 4814529 A	21-03-1989
DE 4330354	A	09-03-1995	DE 4330354 A1	09-03-1995
			WO 9507304 A1	16-03-1995
US 2448260	A	31-08-1948	NONE	
EP 211819	A	25-02-1987	US 4654179 A	31-03-1987
			AT 63319 T	15-05-1991
			AU 581091 B2	09-02-1989
			AU 5943386 A	08-01-1987
			CA 1267260 A1	03-04-1990
			DE 3679117 D1	13-06-1991
			EP 0211819 A1	25-02-1987
			JP 1941392 C	23-06-1995
			JP 6069706 B	07-09-1994
			JP 62009928 A	17-01-1987
			MX 163294 A	13-04-1992
US 5955619	A	21-09-1999	CH 686306 A5	29-02-1996
			US 5814692 A	29-09-1998
			US 5773631 A	30-06-1998
			US 6346630 B1	12-02-2002
			AT 404941 B	25-03-1999
			AT 176994 A	15-08-1998
			BE 1008613 A4	04-06-1996
			BR 9403589 A	16-05-1995
			CA 2132131 A1	18-03-1995
			CN 1106809 A ,B	16-08-1995
			CN 1191229 A ,B	26-08-1998
			CZ 9402263 A3	12-04-1995
			DE 4432732 A1	23-03-1995
			ES 2112140 A1	16-03-1998
			FR 2710063 A1	24-03-1995
			GB 2281910 A ,B	22-03-1995
			HK 1005619 A1	15-01-1999
			IT MI941891 A1	17-03-1995
			JP 3023586 B2	21-03-2000
			JP 7233160 A	05-09-1995
			NL 9401507 A	18-04-1995
			RU 2134689 C1	20-08-1999
			SE 9403091 A	18-03-1995
			SG 52428 A1	23-05-2000
			SK 110594 A3	07-06-1995
			US 5516920 A	14-05-1996

Information on patent family members

PCT/EP 02/03218

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 891989	A	20-01-1999	DE	19730629 A1	21-01-1999
			EP	0891989 A1	20-01-1999